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IBM RESEARCH LAB SAN JOSE CALIF

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WORKSHOP ON RECENT EXPERIMENTAL AND THEORETICAL APPROACHES TO T--ETC(U)

1980 D HENDERSON, L BLUM, R FAWCETT

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**AFOSR-TR- 81 - 0020** FINAL REPORT

**Workshop on Recent Experimental and Theoretical  
Approaches to the Study of the Electrical Double Layer**

CHAIRMAN: DOUGLAS HENDERSON  
International Business  
Machines Corporation

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*F49620-80-C-0062*

Abstract: This is a report on a workshop sponsored by AFOSR, ONR and the IBM Corporation, convened at the IBM Research Laboratory in San Jose, California, July 23-25, 1980. A small group of scientists interested in fundamental and applied problems related to the electrical double layer were brought together. The workshop consisted of twelve reviews and a panel discussion. The report includes specific recommendations for future work. A program and list of participants are attached.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This is a report on a workshop sponsored by AFOSR, ONR and the IBM Corporation, convened at the IBM Research Laboratory in San Jose, California, July 23-25, 1980. A small group of scientists interested in fundamental and applied problems related to the electrical double layer were brought together. The workshop consisted of twelve reviews and a panel discussion. The report includes specific recommendations for future work.		

## INTRODUCTION

The study of the electrical double layer is important in at least three areas, namely: electrochemical technology, including corrosion, electroplating, batteries, fuel cells, and catalysis; colloid science; and biological science, especially the control of the structure and permeability of membranes.

In view of the importance of this subject, a workshop was convened whose purpose was to bring together a small group of scientists interested in problems related to the electrical double layer from both fundamental and applied points of view. Forty-four attendees from North America, Latin America, Europe and Australia participated in discussions related to the most recent advances in the subject area. The workshop was held during three days, June 23-25, 1980 at the IBM Research Laboratory in San Jose, California.

Twelve reviews of forty minutes duration were presented. Each presentation was followed by thirty minutes of lively discussion. It was apparent at the outset that there were significant differences between the theorists and experimentalists in philosophy and scientific vocabulary. However, by the end of the workshop significant progress had been made toward bridging this gap. The two groups were largely talking the same language and had been made aware of relevant theoretical and experimental problems in the field. The theorists left the workshop with a keener awareness of and interest in the role of solvent, particularly at the interface. On the other hand, the experimentalists saw the need to obtain data for systems which would clearly demonstrate important physical

phenomena.

#### PROGRAM OF THE WORKSHOP

The first morning opened with overview talks by Henderson and Parsons. Henderson summarized the philosophy and the methods used by the theorists. Parsons surveyed experimental results and emphasized the importance of the structure of the solvent at the interface. He also mentioned the difficulties in observing deviations from the Gouy-Chapman theory of the diffuse layer.

The afternoon of the first day was devoted to discussions of specific theoretical methods. Valleau outlined the Monte Carlo method and the problems associated with long range electrical forces. He presented results for the diffuse layer which can be used in assessing theoretical methods. Blum discussed analytical methods with particular emphasis on the treatment of a discrete solvent. Outhwaite presented his recent calculations based on the modified Poisson-Boltzmann equation.

The second day was largely devoted to experimental results. Bewick discussed reflection spectroscopy (both infra-red and Raman) and presented some new and remarkable results for infra-red spectra which show great promise for the study of the solution immediately at the interface. Trasatti presented a systemization of data which illustrated the influence of the nature of the metal on the interaction of solvent molecules with the electrode.

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In the afternoon, Fawcett presented a review of approximate treatments of the structures of solvent monolayers and showed how these approximations can be used to understand interfacial capacitance measurements in a variety of non-aqueous solvents. Levine presented a continuum dielectric treatment of ionic adsorption. The afternoon session concluded with Hubbard's presentation of physical ultra high vacuum methods for examining the specific interaction between solvent molecules and metals. These methods are particularly sensitive to structure.

Wednesday morning's session was devoted to double layers in colloidal systems. Chan discussed the importance of ionic double layers in colloidal suspensions and described theoretical and experimental investigations of the interaction of overlapping double layers. Snook discussed phase transitions in colloidal systems and outlined his computer simulations of overlapping double layers. He also described a photon correlation technique for examination of the dynamics of these systems. At the banquet, Eyring discussed the role of water in biological systems. On Monday evening, an informal discussion was organized and included presentations by Macdonald, Beck, Mohilner, Perram and Taraszewska.

#### CONCLUSION AND RECOMMENDATIONS

The meeting closed with a general discussion initiated by a panel consisting of Parsons, Conway, Vallean, McQuarrie, Trasatti and chaired by Parsons. It was the general consensus that for simple systems, the

Chapman-Stern theory adequately describes the interfacial capacitance. However, the theorists pointed out that this theory did not accurately predict the potential profile. There is some experimental support for this point of view from studies of electrode kinetics. The problem of how one should deal with the effect of image forces was raised, but while it was felt to be important, it was not evident how one should proceed.

In general, the effect of the properties of the electrode material on the structure of the electric double layer needs further theoretical and experimental study. Also, there was some discussion that some solvent other than water might be appropriate for a comparison of theory and experiment although the view was strongly expressed that the major effect should be concentrated on water in view of its overwhelming importance. It was also pointed out that in technological systems, solutions of high concentration containing asymmetrical and mixed electrolytes are important. These are the very conditions at which the newer theoretical approaches are likely to be more satisfactory than the Chapman theory. Further work in these areas should be pursued.

The theorists strongly expressed the view that if theory was to be truly effective, it must be developed rigorously, even though this could be a slow process.

Some specific recommendations are:

- (1) Experimentalists and theorists should combine their efforts so that theories are presented in a form which can be compared with

experiment. Experimentalists must devise new methods which will permit critical tests of theory. This workshop was a valuable first step toward these goals.

- (2) The new theoretical approaches should be extended to include the effect of the solvent, especially near the interface.
- (3) Asymmetric and high concentration electrolytes should be examined using both theoretical and experimental methods.
- (4) New methods, such as the spectroscopic and surface physical methods should be strongly supported as these are most likely to lead to critical tests of theoretical descriptions.
- (5) There should be a reassessment in three to five years in the form of a workshop, which might also include representatives from solid state science provided that the size of the meeting is not unduely increased thereby. This meeting was effective because of its limited size and careful selection of participants which promoted stimulating and effective discussion in which nearly all of the confereees participated.



# APPENDIX I - PROGRAM

Monday, June 23, 1980

Morning Introductory Session, Chairman: B. Conway

9:00 a.m.	R. Kay	Welcome
9:10 a.m.	D. Henderson	Overview of Statistical Mechanical Methods
10:20 a.m.	Break	
10:40 a.m.	R. Parsons	Overview of Experimental Evidence
11:50 a.m.	Lunch	

Afternoon Session on Specific Theoretical Methods, Chairman: W. Olivares

1:00 p.m.	J. Valleau	Computer Simulations
2:20 p.m.	Break	
2:30 p.m.	L. Blum	Integral Equations--Analytical Methods
3:40 p.m.	Break	
3:50 p.m.	C. Outhwaite	Integral Equations--Numerical Methods
5:00 p.m.	Return to Hotel	

Evening - Informal Discussions, Board Room

Tuesday, June 24, 1980

Morning Session on Specific Experimental Methods, Chairman: D. Kolb

9:00 a.m.	A. Bewick	New Experimental Methods in Double Layer Studies
10:10 a.m.	Break	
10:30 a.m.	S. Trasatti	The Role of the Metal
11:40 a.m.	Lunch	

Afternoon Session on Specific Experimental Methods and Adsorption  
Chairman: J. Harrison

1:00 p.m.	R. Fawcett	The Role of the Solvent
2:10 p.m.	Break	
2:20 p.m.	S. Levine	Adsorption--Theoretical Aspects
3:30 p.m.	Break	
3:40 p.m.	A. Hubbard	Adsorption---Experimental Aspects
5:00 p.m.	Return to Hotel	
6:30 p.m.	Social Hour, Board Room	
7:30 p.m.	Banquet	Speaker: Henry Eyring

Wednesday, June 25, 1980

Morning Session on Colloidal Systems, Chairman: D. McQuarrie

9:00 a.m.	D. Chan	Overview
10:10 a.m.	Break	
10:30 a.m.	I. Snook	Computer Simulation
11:40 a.m.	Lunch	

Afternoon

1:00 p.m.	Round Table Discussion
3:30 p.m.	Coffee
4:00 p.m.	Return to Hotel

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